

Slow stress relaxation in randomly disordered nematic elastomers and gels

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Randomly disordered (polydomain) liquid crystalline elastomers align under stress. We study the dynamics of stress relaxation before, during and after the Polydomain-Monodomain (P-M) transition. The results for different materials show the universal ultra-slow logarithmic behaviour, especially pronounced in the region of the transition. The data is approximated very well by an equation $\sigma(t) \sim \sigma_{eq}(\varepsilon) + A/(1 + \alpha \log t)$. We propose a theoretical model based on the concept of cooperative mechanical resistance for the re-orientation of each domain, attempting to follow the soft-deformation pathway. The exact model solution can be approximated by compact analytical expressions valid at short and at long times of relaxation, with two model parameters determined from the data.

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Liquid crystalline ordering in a confined, randomly quenched geometry has been the subject of considerable research in recent years. Non-aligned polymer-stabilised or dispersed liquid crystals and, in particular, the nematics in aerogels or other porous media [1–3] have been studied with an eye on the universal properties of systems with weak random fields. The basic scaling observation, that at long length scales the static random fluctuations dominate over the dynamic thermal fluctuations, has been verified by rigorous theoretical analysis and experimental studies of correlations and susceptibilities in a wide variety of systems [4]. The critical slowing down of all relaxation processes in systems with a random, glass-like order is also a well-established universal phenomenon [5,6], with a characteristic stretched-exponential or power-law behaviour as opposed to a normal exponential relaxation of overdamped ordered systems. Accordingly, it has not been surprising to find slow relaxation modes in randomly confined nematic liquid crystals [3,7,8]. However, although the concept of a random orientational effect imposed by the large amount of inner surfaces seems intuitively correct, the direct application of continuum random-field models to systems with strong anchoring on sub-micron length scales is more difficult.

Nematic elastomers and gels have been a focus of extensive recent research for a number of different, but equally compelling reasons. In these systems the liquid crystal ordering and director are coupled to the mechanical degrees of freedom – stresses and strains of the underlying polymer network. As a result, local elastic torques are unbalanced and the non-symmetric Cosserat-like elasticity leads to a number of unique physical effects such as soft elasticity and mechanically-driven orientational switching (see the review [9] for details). It has been argued that the network crosslinks could act as local sources of quenched disorder and the nematic gel is analogous to the spin glass with random magnetic anisotropy [10]. The application of external stress to (polydomain) nematic networks disordered on large scales results in a critical transition into the aligned state with an increasing degree of long-range order. This polydomain-monodomain (P-M) transition, analogous to the spin-glass alignment by magnetic field,

has been studied experimentally in some detail [11], confirming that the alignment proceeds via the reorientation of correlated regions (‘domains’) rather than the growth of the favoured ones. Because the polymer chains within each domain are anisotropic, the rotating director causes shape changes, Fig.1, and thus the materials can accommodate the external deformation without significant stress response. In this Letter we study the dynamics of this transition by increasing the extensional strain ε in controlled small steps and monitoring the relaxation of stress $\sigma(t)$.

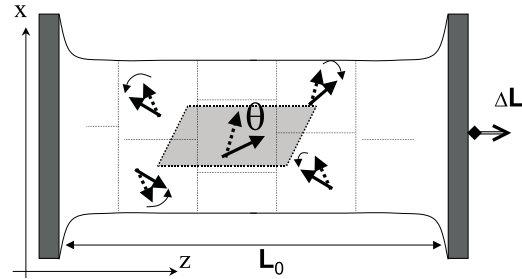


FIG.1 Schematic illustration of a stretched polydomain elastomer. As each correlated domain rotates its director towards the extension axis, its shape is changing. The shear strain associated with the rotation θ (indicated by shading of a single domain) needs to be compatible with the surrounding elastic medium.

We find this relaxation to be extremely slow, increasingly so in the vicinity of critical stress for the P-M transition, and following the logarithmic law over several decades of time. Similar logarithmic decays have been observed in other systems, as different as nematics in silica gels [7] and avalanches at the angle of repose [12], and are reminiscent of the $1/f$ noise kinetics [13]. We propose a theoretical model for a rate constant vanishing with an essential singularity due to the cooperative mechanical barriers for each domain’s rotation. The resulting kinetic equation, having a form $\dot{\theta} = -m\theta^3 e^{-u/\theta}$, gives a solution which at short times resembles the power-law $t^{-1/2}$ and at long times can be approximately interpolated as $1/(1 + 2 \log t/t^*)$, with the crossover time $t^* = (mu^2)^{-1}$. Both regimes correspond well to the experimental results. We expect this behaviour to be universal across the randomly disordered systems where, as in nematic elastomers and gels,

the relevant order parameter is coupled to the elastic modes: the mechanical compatibility requires the cooperative nature of elastic barriers.

The materials used in this experiment are three different types of side-chain liquid crystalline polymers: polysiloxanes [14] crosslinked via rather flexible tri-functional groups, polyacrylates crosslinked by bi-functional chemical groups [15] and by γ -radiation [16]. All materials had slightly different crosslinking density, around 5-10%. The backbone anisotropy is very different for siloxane and acrylate chains, the anisotropy of chain radii of gyration being $R_{\parallel}/R_{\perp} \approx 1.6$ and 1.06, respectively (for Gaussian polymers $\langle R_{\parallel,\perp}^2 \rangle = \frac{1}{3} \ell_{\parallel,\perp} L$ with L the chain contour length). The glass transition temperature for polysiloxane elastomer was around -5C (with nematic-isotropic transition $T_{ni} \sim 42$ C), while the polyacrylates become glasses at $T_g \sim 50$ C (with $T_{ni} \sim 110$ C) [17]. Hence the experiment was carried at 30C for polysiloxane elastomer and at around 90C for both polyacrylates. In spite of all these differences, the results obtained are distinctly similar and in this Letter we concentrate mostly on the polysiloxane system, which has more dramatic quantitative effects due to the higher chain anisotropy. The experimental approach is straightforward. Strips of polydomain nematic rubber ($\sim 15 \times 5 \times 0.3$ mm) were suspended on a stress gauge and extended in controlled strain fashion in a box which was thermostatically controlled. We applied a consecutive fixed-step extensions of ~ 0.5 mm every 24 hours (thus providing an effective strain rate of $\dot{\epsilon} \sim 3 \cdot 10^{-7} \text{s}^{-1}$). The data for variation of response force with time has been collected and then converted to the nominal stress σ (and the extension – to engineering strain $\epsilon = \Delta L/L_0$). The question of temperature control required a serious attention. The accurate measurement of very small changes in stress over large time intervals demanded the experimental error to be brought down to 0.05% in stress and 0.1° in temperature. The partially and fully aligned nematic elastomers are very thermally sensitive. We, therefore, included an additional correction to account for this effect.

The stress-strain dependence of polysiloxane nematic rubber, going through the P-M transition is shown in Fig.2. The sets of data points shown are collected at fixed intervals of 20s, 100s, 500s and 24 hours after the strain increment from the previous-day value. One clearly sees the major trend of the P-M transition, exhibited at all times: When the threshold stress is reached, the correlated nematic domains begin to rotate towards the direction of extension. Because the average polymer backbone is prolate along the local nematic director \mathbf{n} , the aligning of average \mathbf{n} results in the effective lengthening of the whole sample, thus accommodating the imposed strain and creating the stress plateau over a large interval of deformations. The strain at the end of the equilibrium stress plateau is determined by the anisotropy of chain shape R_{\parallel}/R_{\perp} . However, the question of what is the equilibrium stress at each value of ϵ requires a detailed analysis of its kinetics. The inset in Fig.2 shows the analogous plot for a chemically crosslinked polyacrylate, with a much smaller backbone

anisotropy and the stress plateau region.

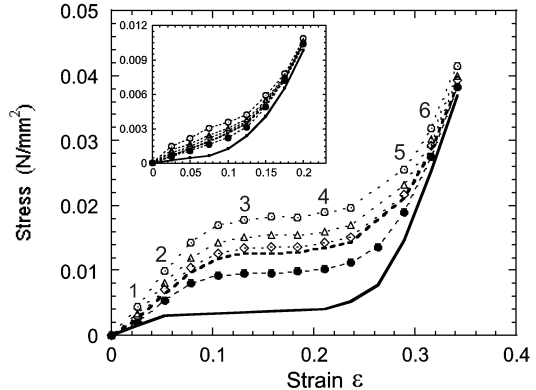


FIG.2 Experimental values of the nominal stress in polysiloxane nematic rubber, as observed at 20s (\circ), 100s (\triangle), 500s (\diamond) and 24 hours (\bullet) after the strain increment. The numbered points correspond to the data sets used in Fig.3. The thick dashed line is the saturation level of 'apparent power-law'; the solid line shows the true equilibrium values $\sigma_{eq}(\epsilon)$ the stress would achieve, if given time for inverse-logarithmic decay to saturate [see Eq.(3) and Fig.4]. The inset shows the same plot for chemically crosslinked polyacrylate.

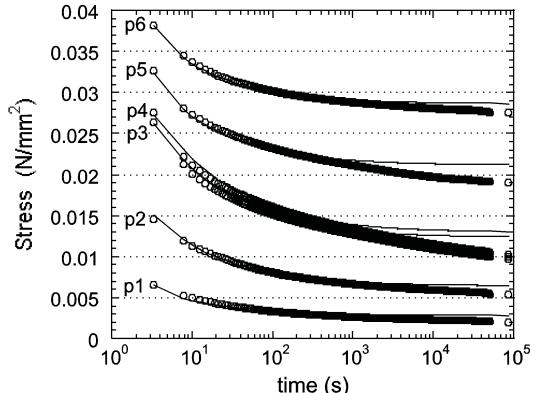


FIG.3 Six selected relaxation plots $\sigma(t)$ for points, labelled from 1 to 6 in Fig.2, in polysiloxane sample. Note, that the plots for points p3 ($\epsilon = 0.13$) and p4 ($\epsilon = 0.21$) are hardly distinguishable, even though they are at each end of the stress plateau. The slow (logarithmic) relaxation at long times is evident, with the slope significantly increasing as the P-M transition is being approached from both sides. Thin solid lines show the 'apparent power law' model, Eq.(3), which fits only the short-time region of each plot.

Fig.3 shows the variation of stress with time after the strain increment for several selected points in Fig.2. The logarithmic scale contracts the long-time region and enhances the effect of decreasing $\sigma(t)$. One immediately recognises the fact that, especially for the points on the stress plateau (*i.e.* during the P-M transition), the equilibrium stress has not been achieved even after the 24-hour interval. Fig.4 gives an example of data analysis. The relaxation of stress at relatively short times accurately follows a power-law with a seemingly universal exponent $-\frac{1}{2}$. This variation has been reproduced in all three different materials (studied at different temperatures), for all points on the stress-strain curve of Fig.2. At longer times a logarithmic decay was evident. Again, this has been a feature for all materials and at all strains, however, the slope of the logarithmic decay was very different, dramatically increasing for the materials with higher chain anisotropy and towards the P-M transition stress plateau. In fact, the logarithmic decay was hard to detect for the first and last points in

Fig.2 for highly anisotropic polysiloxane nematic rubber and, equally, for the chemically crosslinked polyacrylate (which is known to have a very small backbone anisotropy). Finally, the elastomer samples at large deformations (of 10-30% in our study) always develop a distinct necking near the rigid clamps (which do not allow the reduction of sample width required by incompressibility). As a result, even at deformations long past the stress plateau and the samples well-ordered in the middle, there are still polydomain regions near the clamps are in an incomplete state of alignment (this is clearly seen by the eye and under the microscope). Similarly, well before the P-M transition is reached, there are internal processes associated with domain wall localisation [10], also contributing to slow cooperative relaxation. Therefore, it is attractive to attribute the residual logarithmic decay away from the P-M transition to such artefacts of non-uniformity and conclude that the main stress relaxation occurs during the P-M transition and is due to the rotation of correlated nematic domains.

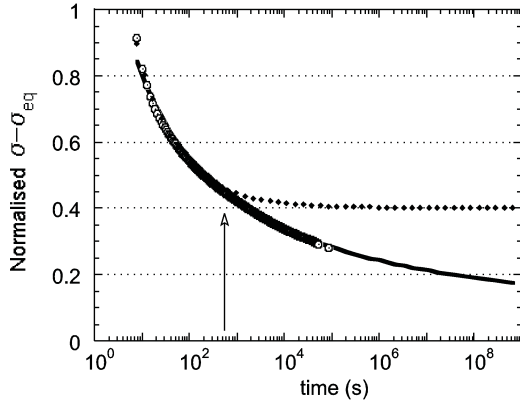


FIG.4 Analysis of relaxation for the point $p4$ (\odot) where the stress has been normalised for convenience to vary between 1 and 0. The ‘apparent power law’ model with the exponent $-\frac{1}{2}$ (dots) fits the data well until the crossover time t^* is reached. A good overall fit of the stress $\sigma(t)$ is given by the inverse-logarithm function $\sigma = \sigma_{eq} + A/(1 + \alpha \log t)$, the solid line.

To understand the results, one needs to recall the basic concepts of soft elasticity in nematic gels (or any other Cosserat-like elastic media with an independent Goldstone degree of freedom); the reader should refer to [9] for details. Considering a region of locally uniform director (a ‘domain’), the rubber-elastic energy can be reduced to zero if the director rotation θ and the Cauchy strain tensor $\underline{\underline{\lambda}}$ are related by the equation $\underline{\underline{\lambda}} = \underline{\underline{\ell}}(\theta)^{1/2} \underline{\underline{\ell}}(0)^{-1/2}$, where the uniaxially anisotropic polymer step-length matrix is given by $\ell_{ij} = \ell_{\perp} \delta_{ij} + (\ell_{\parallel} - \ell_{\perp}) n_i n_j$. For a plane stretching and director rotation as in Fig.1, when the deformation $\varepsilon = \lambda_{zz} - 1$ is applied, the elastic response can be reduced if the director rotates by $\theta \approx \sqrt{2\ell_{\parallel}/(\ell_{\parallel} - \ell_{\perp})} \varepsilon^{1/2}$. To comply with the soft-elasticity pathway, this rotation requires an associated shear $\varepsilon_{zx} \approx \frac{1}{2}(\ell_{\parallel}/\ell_{\perp} - 1) \sin 2\theta$ [9]. Therefore, a given domain subjected to an external extension ε finds itself out of elastic equilibrium, with a director misaligned by θ and the effective energy density $\Delta f \approx \frac{1}{2} \mu (\ell_{\parallel}/\ell_{\perp} - 1)^2 \theta^4$ at small θ , where $\mu \approx n_x k_B T \sim 10^5 \text{ J/m}^3$ is the rubber modulus. The relaxation of stress

then proceeds via the director rotation towards its soft-elasticity equilibrium, $\Delta\sigma(t) \sim \mu(\ell_{\parallel}/\ell_{\perp} - 1)\theta(t)$, while the dynamics of θ is controlled by the standard model-A equation $\dot{\theta} = -\tilde{m}\theta^3$. Note the cubic force, which is the direct consequence of soft elasticity and leads to the power-law decay $\theta = (2\tilde{m}t + \frac{1}{\theta_0^2})^{-1/2}$, where the initial misalignment θ_0 is the function of strain step. This power law is indeed observed at early stages of relaxation for all materials and deformations studied. However, the long-time logarithmic behaviour requires a more delicate analysis.

So far we have discussed the soft response of an individual domain. Surrounded by its neighbours, each of which has its own director and a different set of soft strains, any given domain will face an elastic barrier for its relaxation. In an extreme situation when all neighbouring domains are already aligned and cannot find any soft pathway to accommodate the external strain, the shear deformation of the given domain will not be allowed by mechanical compatibility and no relaxation would occur [18]. Therefore, for each individual domain to relax its local stress, one requires a cooperation of its neighbours, providing a ‘gap’ for the required set of strains. We shall approximate this effect by estimating the effective rate constant \tilde{m} of escape over the average non-soft barrier. Let us first introduce the *mean* angle $\langle\theta(t)\rangle$, the average of misalignment angles of all different domains and thus the measure of non-relaxed part of the stress. As $\langle\theta\rangle$ decays to zero after each strain increment, the total barrier in the system increases as $\langle\theta_0\rangle - \langle\theta(t)\rangle$ with the initial condition $\langle\theta_0\rangle$ proportional to the strain step. If we assume that this energy is evenly distributed between all non-relaxed domains (the number of which is $\propto \langle\theta\rangle$), the effective escape rate becomes $\tilde{m} \sim \exp[-\beta v \frac{\langle\theta_0\rangle - \langle\theta\rangle}{\langle\theta\rangle}]$, leading to the dynamical equation

$$\frac{d}{dt} \langle\theta\rangle = -m e^{-u/\langle\theta\rangle} \langle\theta\rangle^3 \quad (1)$$

(with a small re-arranging of constants). We expect the parameter u to be proportional to the strain step and to the overall strain ε , which is a practical measure of the P-M transition, Fig.2. Both m and u should also be proportional to the chain anisotropy $(\ell_{\parallel}/\ell_{\perp} - 1)$. Eq. (1) integrates for times between zero and t and gives

$$t = \frac{1}{m u^2} \left(\frac{u - \theta}{\theta} e^{u/\theta} - \frac{u - \theta_0}{\theta_0} e^{u/\theta_0} \right); \quad (2)$$

$$\theta = \frac{u}{1 + \text{ProductLog} \left[\frac{m u^2 t}{e} - \left(1 - \frac{u}{\theta_0} \right) e^{-1+u/\theta_0} \right]}$$

with the direct solution $\theta(t)$ expressed via the special function $\text{ProductLog}[z]$, a solution for w of $z = w e^w$ (we have omitted the $\langle \cdot \rangle$ notation for the mean angle θ). The constant in its argument is $\approx 1/e$ at expected $u/\theta_0 \ll 1$. It is straightforward to plot the solution (see Fig.5) and verify that the essential singularity in the rate constant at $\theta \rightarrow 0$, Eq. (1), results in a critical slowing down of the long-time decay.

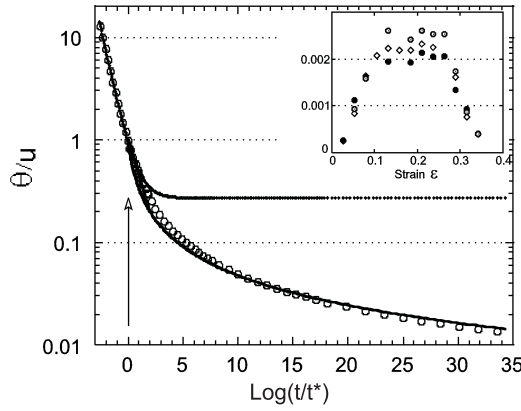


FIG.5 The log-log plot of scaled solution θ/u against scaled time $t/t^* = m u^2 t$, as suggested by Eq.(2), circles. The arrow shows the position of crossover time with two approximate regimes, given by Eqs.(3), shown by dots ('apparent power law') and solid line (inverse logarithm). The inset shows the model activation parameter u vs. ϵ , determined in three ways described in the text: (i) - \diamond , (ii) - \odot and (iii) - \bullet .

There are several qualitative conclusions to be drawn from the Eqs.(1)-(2). At short times, when θ is not small, the exponential in the decay rate is irrelevant and we recover the power-law behaviour $\theta \sim t^{-1/2}$. This 'apparent power law' becomes invalid at a crossover time $t^* \approx (m u^2)^{-1}$ (when $\theta \sim u$), after which the inverse-logarithm function gives an excellent interpolation of the exact solution (2):

$$\begin{aligned} \theta &\approx \frac{1}{(2m t)^{1/2}} + 0.27 u & \text{for } \frac{1}{m \theta_0^2} \ll t \ll t^* \\ \theta &\approx \frac{u}{1 + 2 \log(m u^2 t)} & \text{for } t \gg t^* \end{aligned} \quad (3)$$

The corresponding stress relaxation behaviour, $\sigma(t) = \sigma_{eq} + \text{const} \cdot \theta(t)$ closely reproduces the data, presented in Figs. 3 and 4. The experimental values for crossover time t^* , slope and saturation level of 'apparent power law' and fit of the long-time logarithmic tail provide a sufficient number of independent measurements for each data set to accurately determine the two model parameters, m and u . The inset of Fig.5 shows the variation of parameter u for the polysiloxane sample as function of position on the stress-strain curve, determined by three different methods: (i) using the difference between σ_{eq} and the 'apparent power law' saturation being $\approx 0.27 u$, (ii) identifying the numerator of the long-time inverse-logarithm fit with u and (iii) combining the slope of the 'apparent power law' m and the crossover time for each plot, $u = (m t^*)^{-1/2}$. The plateau value $u \approx 0.0023$ (and the corresponding plateau for the parameter $m \approx 700$) strongly depend on the material and temperature, presumably via the chain anisotropy, but are also approximately linear functions of the small strain step.

Considering some experimental ambiguities (such as the effect of non-uniform necking) and theoretical simplifications, we consider the proposed model to provide a good qualitative description of the data. All three materials show the same type of response, with only parameters m and u reflecting the difference. Much remains to be done to build a full understanding of stress

relaxation phenomena in nematic elastomers with, it appears, the unavoidable effects of quenched disorder. One needs to study the effect of temperature, in particular, close to the nematic transition point T_{ni} . The detailed role of chain anisotropy R_{\parallel}/R_{\perp} remains to be investigated. Correlating the stress relaxation with equilibrium autocorrelation functions, expected to follow the activated scaling [5] as the spin-glasses and random nematics do, would also be desirable. A refinement of the theoretical model is desirable, particularly to address the role of small linear (semi-soft) corrections to the cubic force.

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